



Ultrathin graphitic C_3N_4 nanosheets as highly efficient metal-free cocatalyst for water oxidation

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ABSTRACT

Here, we demonstrate that ultrathin graphitic-phase C_3N_4 nanosheets (g- C_3N_4 -NS) could serve as an efficient metal-free cocatalyst for improving oxygen evolution activity on nanoporous $BiVO_4$ photoanode. More specifically, as compared with pure $BiVO_4$ photoanode, ultrathin g- C_3N_4 nanolayers not only suppress the surface charge recombination of $BiVO_4$, but also effectively transfer and store holes for water oxidation. As expected, the ultrathin graphitic-phase C_3N_4 cocatalyst modified $BiVO_4$ photoanode exhibited significantly improved photocurrent density and H_2 generation capability, nearly 7 and 12 times with respect to the pristine $BiVO_4$ under the same conditions. These results demonstrate an effective approach for the design and construction of low-cost and highly efficient PEC systems.

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1. Introduction

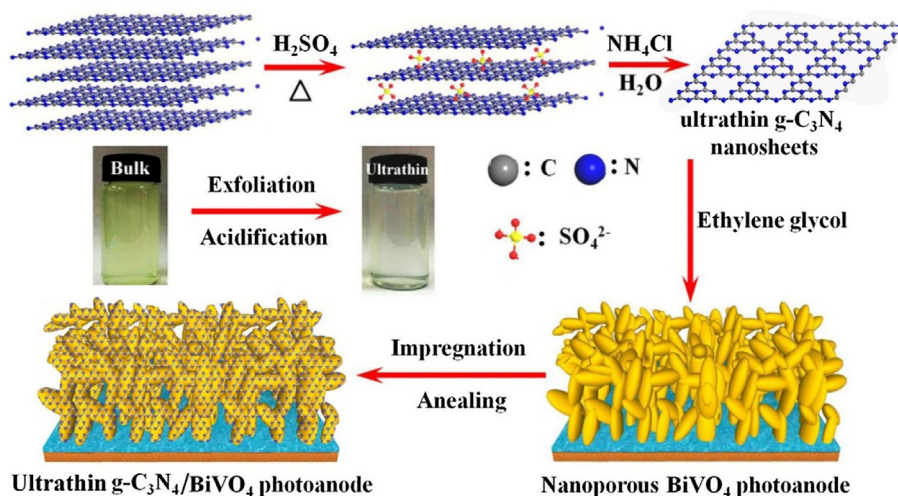
Photoelectrochemical (PEC) water splitting is a potentially scalable approach to store solar energy in the form of clear and renewable H_2 fuel [1–4]. Among various semiconductors, *n*-type monoclinic bismuth vanadate ($BiVO_4$), with a moderate band gap matching well with solar spectrum, has recently emerged as a promising photoanode material for PEC water-splitting [5–13]. However, the PEC performance for water oxidation is far below that expected owing to the intrinsically sluggish kinetics of the oxygen evolution reaction (OER) dominated by photogenerated holes. In this regards, various strategies, including metal ions doping [14–17], hetero-coupling [18–21], and cocatalyst deposition [8–11,22,23], have been extensively employed to improve the performances of $BiVO_4$ -based photoanodes. Particularly, depositing *p*-type VIII metal (Fe, Co, Ni) oxide or (oxy) hydroxide with reversible redox properties, which have been extensively utilized as electrocatalysts for water oxidation, has been proved to be a more effective approach to accelerate the surface charge separation as well as minimize the kinetic over potential [11,24,25]. More specifically, the photogenerated holes could be extracted from the $BiVO_4$ bulk and stored in the *p*-type cocatalysts for suppressing electron-hole recombination. Recently, Gong et al. [22] demonstrated that the loading *p*- Co_3O_4 particles on $BiVO_4$ photoanodes

enables simultaneous enhancement of surface reaction kinetics and bulk charge separation. Gamelin et al. [15] modified *W*: $BiVO_4$ photoanode surfaces with Co-Pi catalyst, which yielded a large cathodic shift (~ 440 mV) in the onset potential for PEC water oxidation. Choi et al. [9–11] reported that the loading *p*-type FeOOH and NiOOH dual-layers onto $BiVO_4$ photoanodes could greatly improve the PEC performances. Domen et al. [23] reported that dual catalysts of CoO_x and NiO loaded $BiVO_4$ photoanodes enables a 1.5% half-cell solar-to-hydrogen efficiency for the water oxidation. Although these *p*-type VIII metal cocatalysts could effectively enhance the PEC properties of $BiVO_4$ photoanodes, but the metallic ions containing materials with perceptive toxicity definitely hampered their further applications. Moreover, their usual large thicknesses or dimensions may block sunlight absorption and prolong the holes transport distances. Thereby, the exploration of novel *p*-type metal-free co-catalysts with ultrathin structures may be an alternative strategy for enhancing the PEC performances of $BiVO_4$ photoanodes.

As a typical *p*-type metal-free semiconductor, graphitic-phase carbon nitride (g- C_3N_4) with a graphite-like layered structure has been extensively applied in photocatalytic hydrogen generation [26–29], degradation of organic pollutants [30–33], electrochemical sensors [34,35], and biomedical imaging [36], owing to its appropriate bandgap (2.7 eV), thermal and chemical stability, and nontoxic properties. However, the applications for water oxidation over g- C_3N_4 have been rarely reported as a result of its relatively low position of valence bands. Furthermore, the direct charge transfer across g- C_3N_4 layer is difficult as a result of the graphite-

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Scheme 1. Schematic illustration of the exfoliation and acidification process for fabricating ultrathin g-C₃N₄ nanosheets and BiVO₄/g-C₃N₄-NS photoanodes.

like layered structure with weak van der Waals force. More recently, both theoretical and experimental studies demonstrated that g-C₃N₄ possesses a unique thickness-dependent bandgap, and ultrathin thick 2D nanosheets can effectively enlarge the bandgap with respect to bulk materials, which is attributed to the well-known quantum confinement effect by shifting the conduction and valence band edges in opposite directions [33,34,37–39]. Moreover, owing to the ultrathin layered structure, the g-C₃N₄ nanosheets demonstrated impressive carrier mobility and were extensively applied in various electronic and optoelectronic devices [40]. Thereby, reducing the bulk 3D g-C₃N₄ into ultrathin 2D nanosheets and coating on photoanodes as co-catalysts may not only facilitate the rapid hole transfer from their contact interfaces, but also enhance the oxygen oxidation capability due to the enlarged valence band.

Herein, we demonstrate a simple ethylene glycol dispersion and impregnation method for uniform coating ultrathin g-C₃N₄ nanosheets (g-C₃N₄-NS) on nanoporous BiVO₄ photoanodes. More specifically, ultrathin g-C₃N₄-NS could effectively suppress the surface charge recombination on the BiVO₄, and photogenerated holes could be effectively stored on their valence band for water oxidation. Nyquist curves further demonstrated that the ultrathin g-C₃N₄ structure could greatly increase the charge-carrier density and facilitate more efficient electron-hole separation. As expected, the ultrathin g-C₃N₄-NS loading BiVO₄ photoelectrodes exhibit superior photoelectrochemical water oxidation in terms of onset potential, photocurrent density and H₂ generation capability as compared with pure as well as metal electrocatalysts modified BiVO₄ electrodes.

2. Results and discussion

Scheme 1 shows the synthesis process of ultrathin g-C₃N₄-NS as well as their coating on nanoporous BiVO₄ photoanodes in this work. Briefly, ultrathin g-C₃N₄-NS was prepared by an acidification oxidation and exfoliation process for bulk g-C₃N₄, and finally dispersed in ethylene glycol solvent [41,42], which is crucial for the subsequent loading on nanoporous BiVO₄ photoanodes. The X-ray diffraction pattern of g-C₃N₄-NS (Fig. S1B) is consistent with the bulk g-C₃N₄, suggesting that the nanosheets basically possess the same crystal structure as the bulk g-C₃N₄. With respect to the bulk g-C₃N₄, the peak originated from the periodic stacking of layers in the nanosheets is shifted from 27.34° to 27.98°, indicating a decreased gallery distance between the nanosheets [27,28]. The

UV–vis absorption spectrum of g-C₃N₄-NS (Fig. S2A) clearly shows an obvious blue shift of the intrinsic absorption edge with respect to the bulk g-C₃N₄. The derived bandgap from the plot versus the energy of the absorbed light (Fig. S2B) is 3.03 eV for the ultrathin nanosheets, which is larger than the bulk material of 2.75 eV. The band structure of g-C₃N₄ and pure BiVO₄ has been tested and calculated. Besides, the band structure of the heterostructure has been shown in Fig. S3.

Fig. 1A shows the typical transmission electron microscope (TEM) image of the BiVO₄/g-C₃N₄-NS sample. The nanoporous BiVO₄ photoanodes have been coated by ultrathin g-C₃N₄ nanolayers, and no evident bulk structure as a result of self-agglomeration have been observed. The high resolution TEM image in **Fig. 1B** exhibits that ultrathin g-C₃N₄ nanolayers with a thickness of 2 nm have been compactly attached on the surfaces of monoclinic BiVO₄ nanocrystals. Moreover, both carbon and nitrogen elements were detected in the whole regions from the elemental mapping images (**Fig. 1C**) and elemental line scanning (**Fig. S4**), which confirm the uniform dispersion of a g-C₃N₄ nanolayers on the surfaces of nanoporous BiVO₄. However, as compared with pure nanoporous BiVO₄ sample as shown in **Fig. S5**, the SEM images (**Fig. 1D** and **E**) and XRD patterns (**Fig. 1F**) demonstrated no evident crystals structure or morphology change, which should be due to the uniform dispersion and ultrathin thickness of g-C₃N₄ nanosheets. Besides, the fourier transform infrared (FT-IR) spectra have also been performed. As shown in **Fig. S6**, the basic peaks of g-C₃N₄ have been clearly observed in the as-prepared samples [29,33]. The UV–vis diffuse reflectance spectra (DRS) were utilized to investigate the band gap energy (E_g) values of the crystals (**Fig. S2**). As a result of large direct bandgap energy (3.03 eV) of ultrathin g-C₃N₄-NS, the absorption edge and intensity of BiVO₄/g-C₃N₄-NS are generally consistent with pure BiVO₄ with direct band gap energy (E_g) of 2.48 eV. On the basis of above results, it can be confirmed that ultrathin g-C₃N₄ nanosheets could be successfully and uniformly coated on the BiVO₄ photoanodes by this simple impregnation process.

Fig. 2 shows the high-resolution C1 s and N1 s spectra of g-C₃N₄-NS and BiVO₄/g-C₃N₄-NS. The C1 s spectra (**Fig. 2A**) shows two deconvoluted peaks at 288.6 eV and 284.8 eV, ascribed to the signals of sp²-bonded carbon (N–C=N) and standard reference carbon, which is usually observed in the XPS spectrum of carbon nitrides. In **Fig. 2B**, the high resolution N1 s spectra can be also deconvoluted into three different peaks. The N1 s peak at 398.9 eV corresponds to sp² hybridized aromatic N bonded to carbon atoms (C=N–C). The peak at 399.7 eV is assigned to the tertiary N bonded to carbon

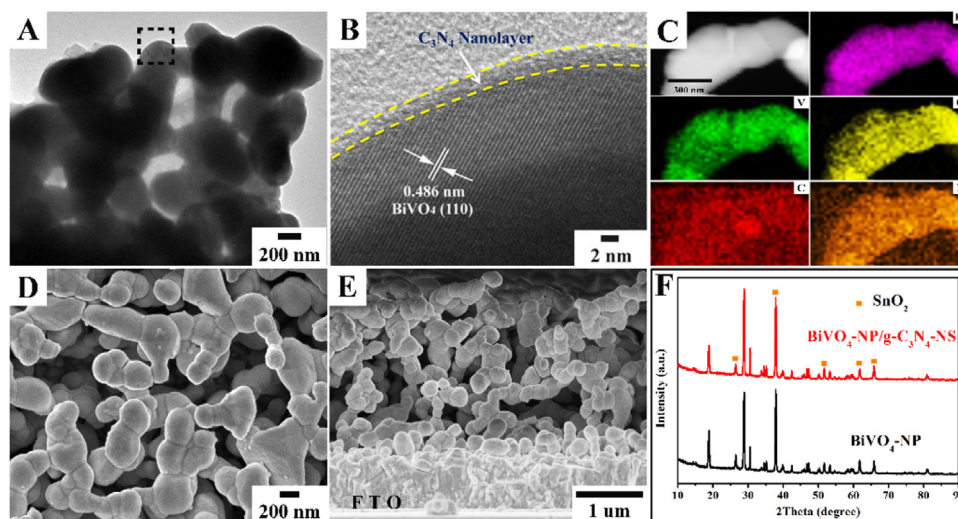


Fig. 1. TEM (A), HRTEM (B) and the corresponding elemental mappings (C) images of BiVO₄/g-C₃N₄-NS. The image in (A) is taken from the region marked with a rectangle in (B). Finally, top (D) and side view (E) SEM images, XRD (F) patterns of BiVO₄/g-C₃N₄-NS.

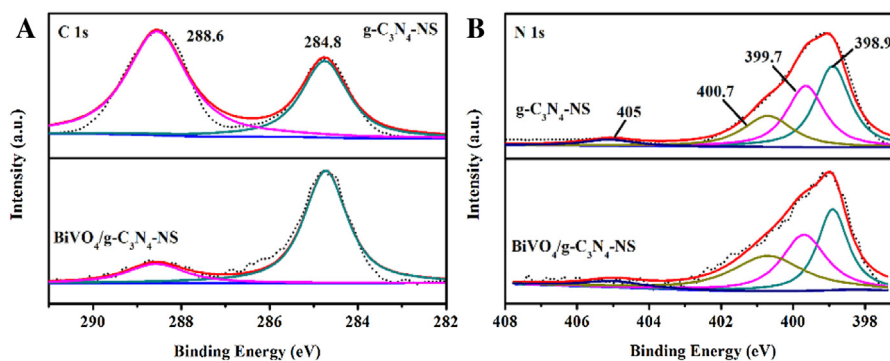


Fig. 2. XPS spectra of g-C₃N₄-NS and BiVO₄/g-C₃N₄-NS: (A) C 1s, (b) N 1s.

atoms in the form of N-(C)₃ or H-N-(C)₂. The peak with a high binding energy at 400.7 eV is attributed to quaternary N bonded to three carbon atoms in the aromatic cycles [43,44]. And the very weak peak at 405 eV corresponds to the π excitations [45,46]. Combining with the above results, except for the peaks intensity, the bonding characteristics of C 1s and N 1s have no apparent change between g-C₃N₄-NS and BiVO₄/g-C₃N₄-NS photoanodes.

Fig. 3 shows the typical current-potential curves of BiVO₄, BiVO₄/g-C₃N₄-NS, and BiVO₄/bulk g-C₃N₄ under visible light ($\lambda \geq 420$ nm) in 0.1 M Na₂SO₄ electrolyte. The BiVO₄/g-C₃N₄-NS provides a photocurrent density of 3.12 mA/cm² at 1.23 V vs. RHE, which is about 7 and 4 times higher than those of BiVO₄ (0.45 mA/cm² at 1.23 V vs. RHE) and BiVO₄/bulk g-C₃N₄ (0.76 mA/cm² at 1.23 V vs. RHE), respectively. The enhanced photocurrent density of BiVO₄/g-C₃N₄-NS photoanode can be attributed to the efficient charge separation as well as holes transfer between BiVO₄ and g-C₃N₄-NS. However, for the bulk g-C₃N₄, the direct charge transfer across bulk layers are very difficult, the photogenerated holes from BiVO₄ would accumulate on their contact interfaces, exhibiting poor surface reaction kinetics for water oxidation. Furthermore, the traditional metal cocatalysts modified BiVO₄ photoanodes have also been prepared according to the previous reports, and compared with the ultrathin g-C₃N₄-NS loaded BiVO₄ photoanode under the same conditions. In the case of CoPi and FeOOH, the photocurrent densities of BiVO₄ photoanodes could be increased up to 1.4 and 1.17 mA/cm² at 1.23 V vs. RHE, respectively, which are much lower than that of BiVO₄/g-C₃N₄-NS

photoanode (3.12 mA/cm²). Fig. 3B shows transient photocurrent response (1.23 V vs. RHE), and we can see that photocurrent densities of BiVO₄/CoPi or FeOOH photoanodes also do not drop or rise dramatically within 200 s, and basically in line with the values of Fig. 3A under the same bias. In addition, the water oxidation kinetics at the interface of the photo-anode/electrolyte was evaluated by electrochemical impedance spectroscopy (EIS) as shown in Fig. 3C [8,22], indicating that a fast charge separation and transfer have occurred in the interfaces between BiVO₄ and g-C₃N₄-NS. According to the previous reports [47,48], two equivalent circuit shown in Fig. S7 are used to fit EIS curves of BiVO₄ and BiVO₄/g-C₃N₄-NS, respectively. Fig. 3D shows hydrogen evolution versus time at the Pt counter electrode for these different photoanodes. The maximum amount of the H₂ generated by the BiVO₄/g-C₃N₄ NS was 121.33 μmol after 150 min. On the contrary, the CoPi, FeOOH and bulk g-C₃N₄ loaded BiVO₄ as well as pure BiVO₄ only produce trace amounts of H₂ (51.29, 42.56, 25.97, and 11.56 μmol) under the same conditions.

On the basis of above results, a possible mechanism for clarifying the charge transfer on BiVO₄/g-C₃N₄-NS has been illustrated in Scheme 2. As a result of the large bandgap ($E_g = 3.03$ eV) of ultrathin g-C₃N₄-NS, only the BiVO₄ could be excited under visible light irradiation, and the photogenerated electrons and holes are formed on the conduction band and valance band, respectively. In the BiVO₄/g-C₃N₄-NS, due to the staggered energy band and superior structure, the photogenerated electrons favorably transfer from the conduction band of BiVO₄ to FTO along the nanoporous structure, which

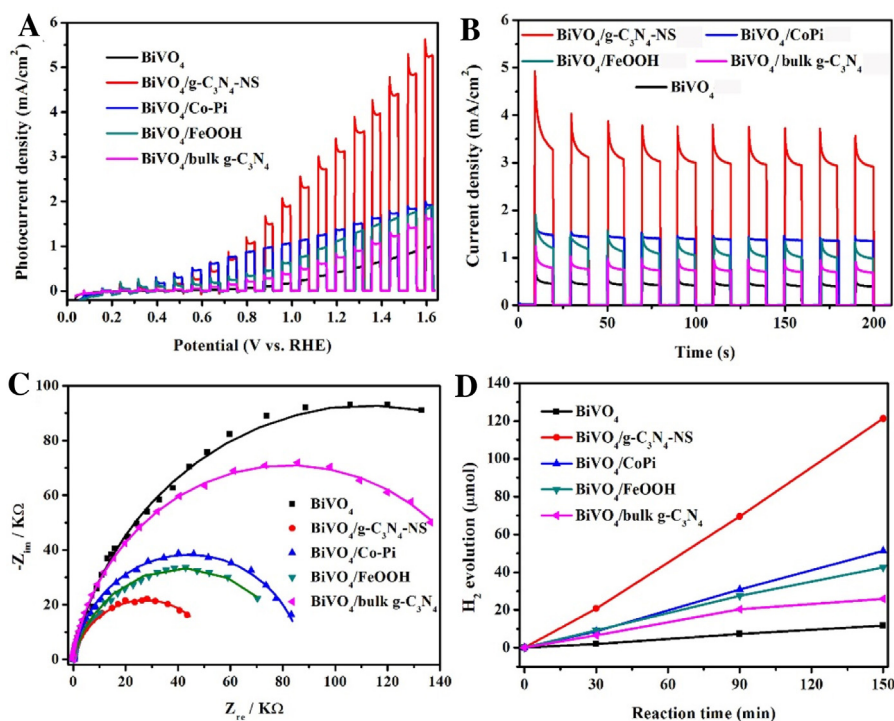
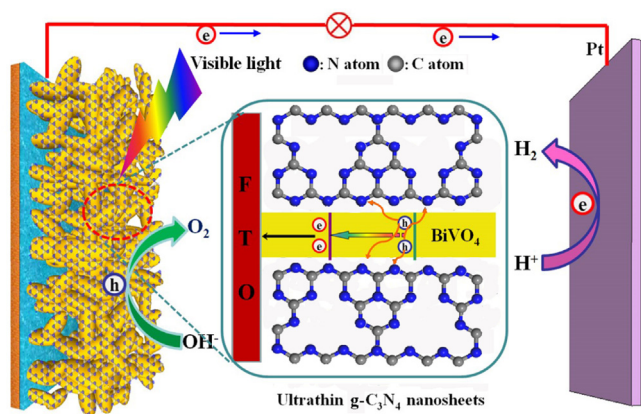


Fig. 3. (A) J-V curves, (B) transient photocurrent response (1.23 V vs. RHE), (C) electrochemical impedance spectroscopy (EIS, solid line is a curve after fitting) and (D) H₂ production for different photoanodes measured with visible-light illumination ($\lambda > 420$ nm) in 0.1 M Na₂SO₄.



Scheme 2. Schematic illustration of the charge transfer in BiVO₄/g-C₃N₄-NS photoanodes.

shorten the travel distance of electron transport and reduce the chance of recombination. Then, the photogenerated electrons move to the Pt electrode via external circuit and reducing water to generate hydrogen. At the same time, the photogenerated holes are transferred from the valence band of BiVO₄ to the valence band of g-C₃N₄-NS, and accumulating in the surface of g-C₃N₄-NS for water oxidation. Notably, the integration of nanoporous and ultrathin film structures possesses short travel distance for photogenerated electron-hole pairs, which contribute to the high PEC activity for water oxidation, and provide enough surface active sites for PEC water oxidation.

3. Conclusion

In summary, we have demonstrated a flexible strategy for rationally constructing ultrathin g-C₃N₄ nanosheets on the surfaces of nanoporous BiVO₄ photoanodes. The ultrathin BiVO₄/g-C₃N₄-NS

photoanode exhibits a high photocurrent density of 3.12 mA/cm² at 1.23 V vs. RHE for water oxidation and H₂ generation capability under visible light ($\lambda \geq 420$ nm) irradiation. The improvement in PEC performance can be attributed to the g-C₃N₄-NS serving as an efficient metal-free cocatalyst owing to its enlarged bandgap (3.03 eV). The ultrathin g-C₃N₄-NS thus effectively promotes the efficient charge separation and holes migration on the ultrathin g-C₃N₄ nanolayer, suppressing the interfacial charge recombination. This work provides an efficient strategy for constructing metal-free cocatalyst on semiconductor photoanodes for improving the PEC activity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.12.014>.

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